

# Geogenic Cr(VI) in groundwater of the Pollino Massif (southern Apennines): occurrence and remediation

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## Abstract

In this study total Cr, Cr(VI), Ni, major and some trace elements were determined in groundwater of northern sector of the Pollino Massif. The investigated area is characterized by ophiolitic rocks consisting of metabasites and cataclastic and highly fractured serpentinites. Two different hydro-facies were observed, reflecting low-temperature water-rock interactions. The Mg-HCO<sub>3</sub> hydrofacies was determined through the weathering of serpentinites, the Ca-HCO<sub>3</sub> groundwater are due to the interaction with calcschist and metabasites. High Cr(VI) concentrations were detected, exceeding the maximum admissible concentrations by Italian regulation, due to the release of Cr(III) from ophiolitic rocks into water and its oxidation to the hexavalent state. Remediation tests were performed at different liquid/solid concentration, and the kinetic data were interpreted with a suitable mathematical model.

**Keywords:** Water-rock interaction, Hexavalent chromium, Remediation test, Serpentinites, Pollino Massif.

## 1. Introduction

The environmental behavior of chromium depends on the valance or oxidation state. Cr(III) is the predominant form in most minerals and is favored by reducing and strongly acidic conditions, while Cr(VI) occurs under oxidizing and alkaline conditions. The Cr oxidation state in the environment is of ecological and public health significance, since Cr(III) is insoluble at pH > 5, immobile and with relatively low toxicity, while Cr(VI) is very soluble, mobile and a human carcinogen. The Italian regulation established a maximum total Chromium and Cr (VI) contaminant level of 50 µg/L and 10 µg/L in drinking water (D. Min. 12/2016). Chromium in subsurface environments originate from both anthropogenic and natural sources. It is mainly produced by manufacturing processes for stainless steel, chrome plating, dyes, pigments and wood preservation. Regarding its natural origin, mineral leaching of ultramafic/ophiolitic rocks can be considered the main geogenic origin of chromium in water. Ultramafic/ophiolitic complexes host Cr mainly in

chromite and silicates (pyroxenes or serpentine) and are widespread in the Mediterranean area (i.e. Italy, Greece, Cyprus, Turkey). In this paper Cr tot, Cr (VI), major and some trace elements were determined in groundwater of northern sector of the Pollino Massif (southern Italy) where the effect of anthropogenic pollution is negligible, in order to verify Cr occurrence and investigate Cr removal by means of innovative adsorbents. Among the most widely applied Cr(VI) remediation technologies, in fact, the most effective and employed for Cr(VI) removal from wastewater is a two-step process, including a first reduction of Cr(VI) species to low-soluble Cr(III) ones and the following sorption and precipitation of both Cr(VI) un-reduced species and Cr(III) species (Vilardi et al., 2019). Though several researchers have already investigated the use of iron-based nanoparticles as reducing agent/sorbent material, real site applications of nano-materials are still limited and more pilot tests are necessary before proceeding to a large diffusion of this technology in environmental remediation.

## 2. The Study Area

The Pollino massif is located in the southern Apennines where the terrains of the ophiolite-bearing Ligurian Complex are largely outcropping. The Ligurian Complex is characterized by two ophiolite-bearing units: the Calabro-Lucanian Flysch Unit and the Frido Unit. The former is made up of non-metamorphic ophiolites, while the Frido Unit is composed of a metasedimentary sequence (phyllites, meta-arenites, quartzites and isolated bodies of meta-limestones or calcschists and metapelites) and blocks of cataclastic and highly fractured serpentinites, metabasalts, metapillow lavas and dismembered metadoleritic dykes (Rizzo et al., 2016; 2018). The Frido unit represent the impermeable unit for most of the springs studied that are located in contact with lower permeability terrains or along fractures.

### 3. Sampling and Analysis

Water samples from 15 springs, owned by both companies and private individuals, used for irrigation and drinking water supply, were collected during a single field trip in May 2018. The most of sampling sites were selected based on previous papers (Margiotta et al., 2012; 2014). All water samples were filtered through 0.45  $\mu\text{m}$  MF-Millipore membrane filters in the field. Cr (VI), Cr<sub>tot</sub>, Ni and other trace elements were determined using graphite tube absorption spectroscopy. Anions and cations were determined by using a Ion chromatograph. Two different nanoparticles, zero-valent iron and magnetite, have been used for Cr(VI) reduction kinetic tests. At each time steps (5 min) the liquid sample was withdrawn, filtered by a Whatman filter (220 nm) and the dyphenylcarbazide method was used to measure the residual Cr(VI) concentration.

### 4. Results and Discussion

The investigated water showed neutral pH (from 6.7 to 7.1), temperature values ranging from 6.0 to 19.1 °C, oxidant redox potentials (from 360 to 600 mV) and electrical conductivity from 230 to 700  $\mu\text{S}/\text{cm}$ . Based on the triangular plots of major anions and major cations (Piper diagram), the waters show Ca and Mg-HCO<sub>3</sub> composition (Fig. 1).

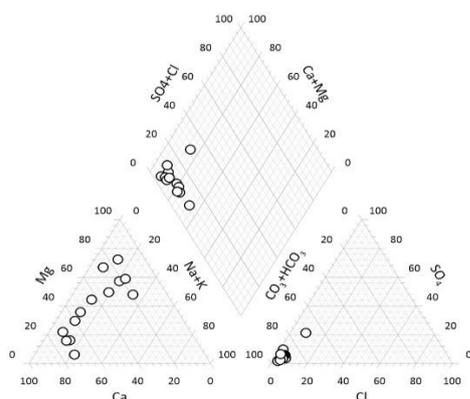


Figure 1. Piper diagram

The concentration of the trace elements (Cr total, Cr VI, Ni, Fe, Zn, Pb, Cu and Al) with the relative maximum admissible concentrations (hereafter MAC) by the Italian legislation (D. Min. 12/2016) are compared in Fig. 2. Cr total concentrations range between 10 and 42  $\mu\text{g}/\text{L}$  and are lower than MAC (50  $\mu\text{g}/\text{L}$ ). Cr VI contents are higher than MAC (10  $\mu\text{g}/\text{L}$ ) and range between 10 and 40  $\mu\text{g}/\text{L}$ . Ni values are generally high (average value of 11.4  $\text{mg}/\text{L}$ ) but lower than MAC (20  $\text{mg}/\text{L}$ ). The other trace elements were generally negligible.

The release of Cr(VI) in groundwaters is mainly due to serpentinite, garnet-rich gneiss dissolution, rocks containing lizardite, antigorite, clinochrysotile, chromium chlorite, magnetite, tremolite, actinolite, pyroxene and calcite. In most of these minerals high Cr(III) concentrations are reported (Dichicco et al., 2015), while its release into solution requires oxidation

to Cr(VI) through the involvement of a comparatively strong oxidant.

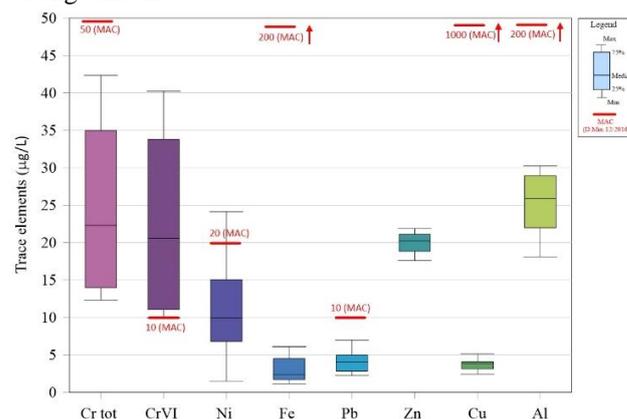


Figure 2. Box and whisker plot of detected trace elements

The groundwater samples were treated with zero-valent iron and magnetite nanoparticles according to a molar ratio with respect to Cr(VI) equal to 1 and 3 mol/mol, (Vilardi et al., 2019). The first nanomaterial was more effective, since after 10 min a Cr(VI) reduction efficiency of 97% has been reached, whereas the second one was characterized by a slower kinetics: an asymptotic value of 84% of Cr(VI) reduction efficiency has been achieved after 75 min of treatment. Results show that both nano-materials showed a notable reducing efficiency towards Cr(VI) species though more tests on pilot scale are necessary before real scale test application.

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